CLAIMS

Claim 1. In a process for producing an olefin by the vapor phase oxidative dehydrogenation of alkane having from 2 to 5 carbon atoms in the presence of molecular oxygen, the improvement comprising, carrying out the vapor phase oxidative dehydrogenation in the presence of an oxidative dehydrogenation catalyst comprising a multimetal mixed oxide having the formula

$$Mn_{\alpha}E^{1}_{\beta}E^{2}_{\gamma}O_{x} \qquad (1)$$

where Mn denotes manganese;

O denotes oxygen;

E^1 represents one or more metal elements selected from the group consisting of phosphorus, arsenic, antimony, boron, sulfur, selenium, tellurium, fluorine, chlorine, bromine, iodine, niobium, tantalum, tungsten, rhenium and copper;

E^2 represents one or more metal elements selected from the group consisting of chromium, iron, cobalt, nickel, silver, gold, zinc, thallium, tin, lead, bismuth, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, yttrium, lanthanum, cerium, neodymium, and samarium; and,

α, β, γ and x denote atomic numbers of Mn, E^1, E^2, and oxygen, respectively, and,

when $\alpha = 1$, $\beta = 0.01\text{-}10$, $\gamma = 0\text{-}5$, and x has a numerical value determined by the state of oxidation of the elements other than oxygen.

Claim 2. The process according to claim 1, wherein, in the oxidative dehydrogenation catalyst of formula (1), when $\alpha = 1$, $\beta = 0.02\text{-}2$ and $\gamma = 0\text{-}1$.

Claim 3. The process according to claim 2, wherein E^1 comprises at least sulfur, and the sulfur is added in the form of its sulfate ion (SO_4^{2-}).

Claim 4. The process according to claim 1, wherein E^1 comprises at least sulfur, and the sulfur is added in the form of its sulfate ion (SO_4^{2-}).

Claim 5. The process according to claim 1, wherein the oxidative dehydrogenation catalyst of formula (1) is one which is dried and fired at temperatures not higher than 300°C.

Claim 6. The process according to claim 1, wherein the oxidative dehydrogenation catalyst is supported on a refractory inorganic carrier.

Claim 7. The process according to claim 1, wherein the oxidative dehydrogenation of said alkane is carried out at a space velocity of from 300 to 30,000 hr^{-1}, and at a temperature of from 250 to 650 °C.

Claim 8. The process according to claim 1, wherein the oxidative dehydrogenation catalyst is selected from the group consisting of $Mn_1Sb_{0.15}O_x$, $Mn_1Sb_{0.25}O_x$, $Mn_1B_{0.1}O_x$, $Mn_1S_{0.1}O_x$, $Mn_1Nb_{0.05}O_x$, $Mn_1W_{0.05}O_x$, $Mn_1Re_{0.05}O_x$, $Mn_1Cu_{0.1}O_x$, $Mn_1Cl_{0.4}O_x$, $Mn_1Sb_{0.15}Cr_{0.1}O_x$, $Mn_1Sb_{0.15}Na_{0.1}O_x$, $Mn_1Sb_{0.15}Mg_{0.1}O_x$, $Mn_1Sb_{0.15}Ce_{0.1}O_x$, $Mn_1S_{0.15}Cr_{0.1}O_x$, $Mn_1Cl_{0.4}Sn_{0.1}O_x$, $Mn_1Sb_{0.15}W_{0.05}Cr_{0.1}O_x$, $Mn_1Sb_{0.15}W_{0.05}S_{0.15}Cr_{0.1}O_x$, and $Mn_1Sb_{0.15}W_{0.05}Nb_{0.05}Cr_{0.1}O_x$.

Claim 9. In a process for producing unsaturated aldehyde and unsaturated acid by the vapor phase oxidative dehydrogenation of C_2 to C_5 alkene in the presence of molecular oxygen, the improvement comprising, carrying out the vapor phase oxidative

dehydrogenation in the presence of an oxidative dehydrogenation catalyst comprising a multimetal mixed oxide having the formula

$$Mn_{\alpha}E^{1}{}_{\beta}E^{2}{}_{\gamma}Ox \qquad (1)$$

where Mn denotes manganese;

O denotes oxygen;

E^1 represents one or more metal elements selected from the group consisting of phosphorus, arsenic, antimony, boron, sulfur, selenium, tellurium, fluorine, chlorine, bromine, iodine, niobium, tantalum, tungsten, rhenium and copper;

E^2 represents one or more metal elements selected from the group consisting of chromium, iron, cobalt, nickel, silver, gold, zinc, thallium, tin, lead, bismuth, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, yttrium, lanthanum, cerium, neodymium, and samarium; and,

α, β, γ and x denote atomic numbers of Mn, E^1, E^2, and oxygen, respectively, and,

when $\alpha = 1$, $\beta = 0.01\text{-}10$, $\gamma = 0\text{-}5$, and x has a numerical value determined by the state of oxidation of the elements other than oxygen.

Claim 10. The process according to claim 9, wherein, in the oxidative dehydrogenation catalyst of formula (1), when $\alpha = 1$, $\beta = 0.02\text{-}2$ and $\gamma = 0\text{-}1$.

Claim 11. The process according to claim 10, wherein E^1 comprises at least sulfur, and the sulfur is added in the form of its sulfate ion (SO_4^{2-}).

Claim 12. The process according to claim 9, wherein E^1 comprises at least sulfur, and the sulfur is added in the form of its sulfate ion (SO_4^{2-}).

Claim 13. The process according to claim 9, wherein the oxidative dehydrogenation catalyst of formula (1) is one which is dried and fired at temperatures not higher than 300°C.

Claim 14. The process according to claim 9, wherein the oxidative dehydrogenation catalyst is supported on a refractory inorganic carrier.

Claim 15. The process according to claim 9, wherein the oxidative dehydrogenation of said alkene is carried out at a space velocity of from 300 to 30,000 hr^{-1}, and at a temperature of from 250 to 650 °C.

Claim 16. The process according to claim 9, wherein the oxidative dehydrogenation catalyst of formula (1) is a catalyst of the following formula (2):

$$Mo_aBi_bFe_cA_dB_eC_fD_gO_x \qquad (2),$$

wherein Mo denotes molybdenum, Bi denotes bismuth, Fe denotes iron, O denotes oxygen,

A represents at least one metal element selected from the group consisting of cobalt and nickel,

B represents at least one metal element selected from the group consisting of alkali metals and thallium,

C represents at least one metal element selected from the group consisting of silicon, aluminum, zirconium and titanium,

D represents at least one metal element selected from the group consisting of tungsten, phosphorus, tellurium, antimony, tin, cerium, lead, niobium, manganese, arsenic and zinc,

a, b, c, d, e, f, g, and x represent the atomic ratios of the respective elements, and, when a = 12, b = 0.1-10, c = 0.1-20, d = 2-20, e = 0.001 = 10, f = 0-30, g = 0-4, and x is a numerical value determined by the state of oxidation of the elements other than oxygen.

Claim 17. In a process for producing unsaturated acid having from 2 to 5 carbon atoms, by the vapor phase oxidative dehydrogenation of the corresponding unsaturated aldehyde of from 2 to 5 carbon atoms, in the presence of molecular oxygen, the improvement comprising, carrying out the vapor phase oxidative dehydrogenation in the presence of an oxidative dehydrogenation catalyst comprising a multimetal mixed oxide having the formula

$$Mn_{\alpha}E^{1}_{\beta}E^{2}_{\gamma}Ox \qquad (1)$$

where Mn denotes manganese;

O denotes oxygen;

E^1 represents one or more metal elements selected from the group consisting of phosphorus, arsenic, antimony, boron, sulfur, selenium, tellurium, fluorine, chlorine, bromine, iodine, niobium, tantalum, tungsten, rhenium and copper;

E^2 represents one or more metal elements selected from the group consisting of chromium, iron, cobalt, nickel, silver, gold, zinc, thallium, tin, lead, bismuth, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, yttrium, lanthanum, cerium, neodymium, and samarium; and,

α, β, γ and x denote atomic numbers of Mn, E^1, E^2, and oxygen, respectively, and,

when $\alpha = 1$, $\beta = 0.01\text{-}10$, $\gamma = 0\text{-}5$, and x has a numerical value determined by the state of oxidation of the elements other than oxygen.

Claim 18. The process according to claim 17, wherein the oxidative dehydrogenation catalyst is represented by the following formula (3):

$$Mo_hV_iW_jE_kF_lG_mH_nO_x \qquad (3)$$

where Mo denotes molybdenum, V denotes vanadium, W denotes tungsten, O denotes oxygen,

E represents at least one element selected from the group consisting of copper, cobalt, bismuth and iron,

F represents at least one element selected from the group consisting of antimony and niobium,

G represents at least one element selected from the group consisting of silicon, aluminum, zirconium, and titanium,

H represents at least one element selected from the group consisting of alkaline earth metals, thallium, phosphorus, tellurium, tin, cerium, lead, manganese and zinc;

h, i, j, k, l, m, n, and x represent the atomic ratios of the respective elements, and, when h=12, i=0.1-10, j=0-10, k=0.1-20, l=0-10, m=0-10, n=0-30, and x has a numerical value determined by the state of oxidation of the elements other than oxygen.

Claim 19. A process for producing unsaturated acid by the vapor phase oxidative dehydrogenation of C_2 to C_5 alkene in the presence of molecular oxygen, which comprises, oxidatively dehydrogenating lower alkene of from 2 to 5 carbon atoms in the vapor phase in the presence of oxidative dehydrogenation catalyst comprising a multimetal mixed oxide having the formula

$$Mn_{\alpha}E^{1}_{\beta}E^{2}_{\gamma}O_{x} \qquad (1)$$

where Mn denotes manganese;

O denotes oxygen;

E^1 represents one or more metal elements selected from the group consisting of phosphorus, arsenic, antimony, boron, sulfur, selenium, tellurium, fluorine, chlorine, bromine, iodine, niobium, tantalum, tungsten, rhenium and copper;

E^2 represents one or more metal elements selected from the group consisting of chromium, iron, cobalt, nickel, silver, gold, zinc, thallium, tin, lead, bismuth, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, yttrium, lanthanum, cerium, neodymium, and samarium; and,

α, β, γ and x denote atomic numbers of Mn, E^1, E^2, and oxygen, respectively, and,

when $\alpha = 1$, $\beta = 0.01\text{-}10$, $\gamma = 0\text{-}5$, and x has a numerical value determined by the state of oxidation of the elements other than oxygen, to produce a mixture of unsaturated aldehyde and unsaturated acid, and

subjecting the unsaturated aldehyde to further vapor phase oxidative dehydrogenation in the presence of oxidative dehydrogenation catalyst of formula (1) to produce the corresponding unsaturated acid.

Claim 20. The process according to claim 19, wherein the oxidative dehydrogenation catalyst used in the oxidative dehydrogenation of said unsaturated aldehyde is represented by the following formula (3):

$$Mo_hV_iW_jE_kF_lG_mH_nO_x \qquad (3)$$

where Mo denotes molybdenum, V denotes vanadium, W denotes tungsten, O denotes oxygen,

E represents at least one element selected from the group consisting of copper, cobalt, bismuth and iron,

F represents at least one element selected from the group consisting of antimony and niobium,

G represents at least one element selected from the group consisting of silicon, aluminum, zirconium, and titanium,

H represents at least one element selected from the group consisting of alkaline earth metals, thallium, phosphorus, tellurium, tin, cerium, lead, manganese and zinc;

h, i, j, k, l, m, n, and x represent the atomic ratios of the respective elements, and, when $h = 12$, $i = 0.1\text{-}10$, $j = 0\text{-}10$, $k = 0.1\text{-}20$, $l = 0\text{-}10$, $m = 0\text{-}10$, $n = 0\text{-}30$, and x has a numerical value determined by the state of oxidation of the elements other than oxygen.

Claim 21. The process according to claim 20, wherein the oxidative dehydrogenation catalyst used for the oxidative dehydrogenation of said alkene to produce said mixture is a catalyst of the following formula (2):

$Mo_aBi_bFe_cA_dB_eC_fD_gO_x$ (2),

wherein Mo denotes molybdenum, Bi denotes bismuth, Fe denotes iron, O denotes oxygen,

A represents at least one metal element selected from the group consisting of cobalt and nickel,

B represents at least one metal element selected from the group consisting of alkali metals and thallium,

C represents at least one metal element selected from the group consisting of silicon, aluminum, zirconium and titanium,

D represents at least one metal element selected from the group consisting of tungsten, phosphorus, tellurium, antimony, tin, cerium, lead, niobium, manganese, arsenic and zinc,

a, b, c, d, e, f, g, and x represent the atomic ratios of the respective elements, and, when a=12, b=0.1-10, c=0.1-20, d=2-20, e=0.001-10, f=0-30, g=0-4, and x is a numerical value determined by the state of oxidation of the elements other than oxygen.